

Novel N-bridging cyclopentadienyl heteropolynuclear organometallamacrocycles with M–Sn (M = Mo or W) bonds

Shan-Shan Chen, Hai-Bin Song, Liang-Fu Tang *

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

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Abstract

Reaction of $\text{PhN}(\text{CH}_2\text{CO}_2\text{Et})_2$ with cyclopentadienyl sodium in a 1:2 ratio yields N-bridging dicyclopentadienyl dianion $[\text{PhN}(\text{CH}_2\text{COCp})_2]^{2-}$, which subsequently reacts with $\text{M}(\text{CO})_6$ to give N-bridging dicyclopentadienyl metal dianions $[\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3)_2]^{2-}$ (M = Mo or W). Treatment of these metal dianions with Ph_2SnX_2 yields tetranuclear heterodimetallic complexes $\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3)_2[\text{SnPh}_2\text{X}]_2$ (X = Cl or Br), while treatment with $\text{CH}_2(\text{SnPh}_2\text{Br})_2$ results in octanuclear heterodimetallic organometallamacrocycles $[\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3)_2]_2[\text{SnPh}_2\text{CH}_2]_2$. All of these new compounds have been characterized by elemental analysis and spectroscopic properties. The crystal structure of complex $[\text{PhN}(\text{CH}_2\text{COCpMo}(\text{CO})_3)_2]_2[\text{SnPh}_2\text{CH}_2]_2$ determined by X-ray crystallography indicates a novel 24-membered organometallic metallamacrocyclic ring system in which four Mo–Sn units are linked by two N-bridging dicyclopentadienyl ligands and two bridging methylene groups.

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1. Introduction

The designed formations of metallamacrocyclic compounds have attracted extensively interest owing to their fascinating structural features, potential application in many aspects such as catalysis, molecular recognition and host–guest interactions [1]. In addition, although various organometallic macrocycles with metal–metal bonds, such as Ga–Ga [2], Rh–Rh [3], Fe–Fe [4], Mo/W–Co [5] and Mo–Fe [6], have been synthesized and characterized, organometallic macrocycles with transition metal–main group metal bonds are rare, especially organotin metallamacrocycles involving metal–metal bonds as integral parts of the molecular architecture [7]. Our investigation on the transition metal–tin bonded heterodimetallic complexes showed that rigid terephthaloyl bridging cyclopentadienyl M–Sn bonded complexes (M = Mo or W) could be used as the

starting materials for the construction of novel heteronuclear organometallic macrocycles [8]. As a continuation of our investigation on heteronuclear metallamacrocyclic complexes with metal–metal bonds for the construction of the rings, we report herein novel N-bridging cyclopentadienyl octanuclear heterodimetallic metallamacrocycles involving transition metal–tin bonds as integral parts of the molecular architecture.

2. Results and discussion

2.1. Synthesis and related reaction of N-bridging cyclopentadienyl metal anions

It is known that properties of the spacer markedly affect the formation of metallamacrocycles. For the comparison of the differences between the flexible N-bridging cyclopentadienyl and the rigid terephthaloyl bridging analogue in the formation of organometallamacrocycles, N-bridging cyclopentadienyl dianion $[\text{PhN}(\text{CH}_2\text{COCp})_2]^{2-}$ was synthesized

* Corresponding author. Fax: +86 22 23502458.

E-mail address: ltang@nankai.edu.cn (L.-F. Tang).

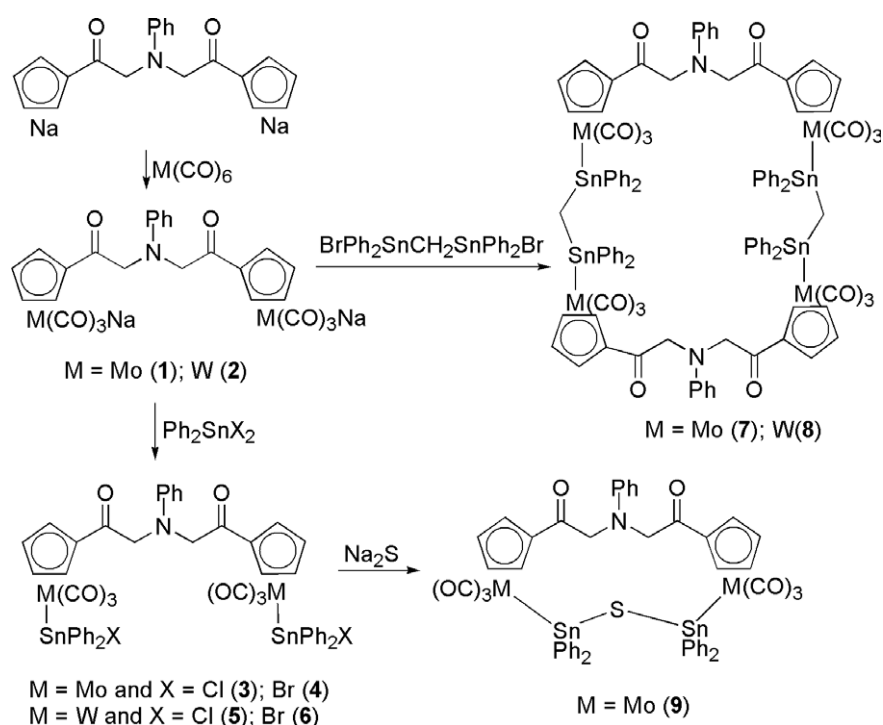
by the reaction of $\text{PhN}(\text{CH}_2\text{CO}_2\text{Et})_2$ with cyclopentadienyl sodium in a 1:2 ratio, which was isolated as a moisture-sensitive sodium salt. Treatment of this salt with $\text{M}(\text{CO})_6$ gave N-bridging cyclopentadienyl metal dianions $[\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3)_2]^{2-}$ ($\text{M} = \text{Mo}$ or W) (Scheme 1), which subsequently reacted with Ph_2SnX_2 yielding exclusively tetranuclear heterodimetallic complexes $\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3\text{SnPh}_2\text{X})_2$ ($\text{X} = \text{Cl}$ or Br), while no cyclic or polymeric products being isolated, similar with the results of the reactions of the rigid terephthaloyl bridging cyclopentadienyl metal dianions $\{[p\text{-(CO)}_3\text{MC}_5\text{H}_4\text{C(O)}_2\text{C}_6\text{H}_4]\}^{2-}$ with Ph_2SnX_2 [7b]. However, upon treatment of these N-bridging cyclopentadienyl metal dianion **1** or **2** with $\text{CH}_2(\text{SnPh}_2\text{Br})_2$, a markedly different reaction took place, which led to a novel 24-membered octanuclear heterodimetallic organometallamacrocyclic complex $[\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3)_2][(\text{SnPh}_2)_2\text{CH}_2]_2$ ($\text{M} = \text{Mo}$ or W), instead of a 14-membered organometallamacrocyclic complex $[\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3)_2][(\text{SnPh}_2)_2\text{CH}_2]$, similar with $[p\text{-C}_6\text{H}_4(\text{COCpM}(\text{CO})_3)_2][(\text{Ph}_2\text{Sn})_2\text{CH}_2]$ [7b]. The change in the reaction pathway is probably attributed to the relative shorter N-containing bridge compared with the terephthaloyl bridge leading to the larger repulsion in $[\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3)_2][(\text{SnPh}_2)_2\text{CH}_2]$. Also as an intriguing result, the reaction of $\text{PhN}(\text{CH}_2\text{COCpMo}(\text{CO})_3\text{SnPh}_2\text{Cl})_2$ with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in refluxing ethanol solution gave a new organometallic metallamacrocyclic complex $\text{PhN}(\text{CH}_2\text{COCpMo}(\text{CO})_3\text{SnPh}_2)_2\text{S}$, similar with the terephthaloyl bridging analog of $\{[p\text{-}[(\text{CO})_3\text{MoC}_5\text{H}_4\text{C(O)}_2\text{C}_6\text{H}_4]\text{-}(\text{Ph}_2\text{Sn})_2\text{S}]\}$ [7b]. In these reactions, the large radius of the

sulfur maybe plays a key role in the formation of these sulfur-bridging metallamacrocyclic complexes.

Complexes **3–9** were air-stable in the solid state and their solution could be manipulated in the air without notable decomposition. They were moderately soluble in chlorinated solvents. These complexes have also been characterized by element analyses and spectroscopic methods. Owing to high symmetry, these complexes show one absorption band of ketone carbonyl in the range of $1694\text{--}1706\text{ cm}^{-1}$, and three typical metal carbonyl stretching bands in the range of $1990\text{--}2015\text{ cm}^{-1}$ in their IR spectra. In addition, their ^1H NMR spectra also exhibit the expected proton signals. For example, two equivalent monosubstituted cyclopentadienyl rings are observed, and their resonances appear as two triplets attributed to overlapped AA'BB' system in the monosubstituted cyclopentadienyl group, and are separated by *ca.* 0.4–0.8 ppm. Their ^{13}C NMR spectra also support the proposed structures. The signal of the ketone carbonyl carbon atom occurs at *ca.* 193 ppm, and three signals of monosubstituted cyclopentadienyl carbons are observed between 88 ppm and 101 ppm.

2.2. The description of crystal structure of 7

The molecular structure of complex **7**, presented in Fig. 1, has been confirmed further by X-ray single crystal diffraction analyses. Selected bond lengths and angles are shown in Table 1. As shown in Fig. 1, complex **7** consists of a novel 24-membered organometallic metallamacrocyclic ring system in which four Mo–Sn units are linked by



Scheme 1. Synthesis and related reactions of N-bridging cyclopentadienyl metal dianions **1** and **2**.

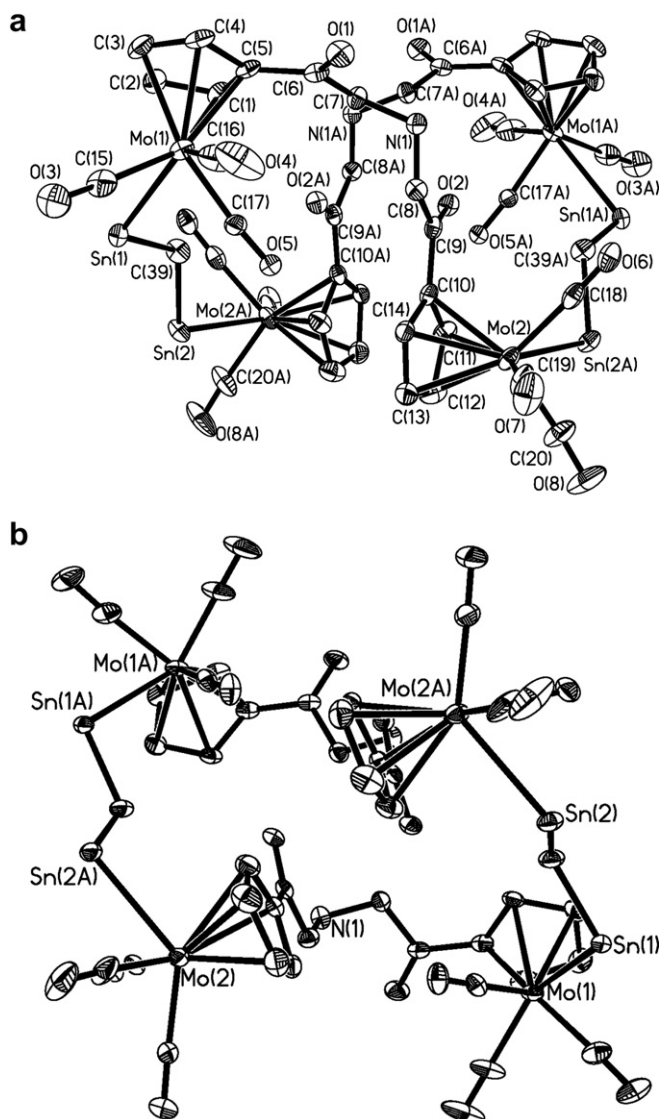


Fig. 1. (a) The molecular structure of complex 7. The thermal ellipsoids are drawn at the 30% probability level. (b) Schematic view of the 24-membered metallacycle conformation. The solvent molecules and the phenyl groups on tin and nitrogen atoms have been omitted for clarity. Symmetric operations of "A" are $1 - x, y, 1.5 - z$.

two N-bridging cyclopentadienyl ligands and two bridging methylene groups, and the Mo–Sn bonds become integral parts of the molecular architecture.

The molybdenum atoms adopt a common 3:4 four-legged piano stool-square pyramidal geometry [9]. The Mo(1)–Sn(1) and Mo(2A)–Sn(2) bond distances are 2.857(1) Å and 2.860(1) Å, respectively, similar with that in the 14-membered terephthaloyl bridging cyclopentadienyl complex $\{p-[(\text{CO})_3\text{MoC}_5\text{H}_4\text{C}(\text{O})_2\text{C}_6\text{H}_4]\{(\text{Ph}_2\text{Sn})_2\text{CH}_2\}\}$ 2.852(1) Å [7b], slightly longer than those in sulfur-bridging cyclopentadienyl complexes (such as in $\{p-[(\text{CO})_3\text{MoC}_5\text{H}_4\text{C}(\text{O})_2\text{C}_6\text{H}_4]\{(\text{Ph}_2\text{Sn})_2\text{S}\}\}$ 2.829(1) Å [7b] and $\{p-[(\text{CO})_3\text{MoC}_5\text{H}_4\text{C}(\text{O})_2\text{C}_6\text{H}_4]\text{Ph}_4\text{Sn}_3\text{S}_3\}$ (2.799(1) Å) [7a]), and longer than those in non-cyclic or small metallacyclic cyclopentadienyl complexes (such as in $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnPh}_2\text{Cl}$ (2.7683(6) Å) [10] and

Table 1
Selected bond lengths (Å) and angles (°) for 7

Bond lengths			
Mo(1)–Sn(1)	2.857(1)	O(2)–C(9)	1.219(10)
Mo(1)–C(17)	1.964(8)	O(3)–C(15)	1.151(12)
Mo(1)–C(16)	1.988(9)	O(4)–C(16)	1.124(11)
Mo(1)–C(15)	2.000(11)	O(5)–C(17)	1.159(10)
Mo(2)–C(20)	1.966(10)	O(6)–C(18)	1.154(11)
Mo(2)–C(19)	1.984(10)	O(7)–C(19)	1.151(11)
Mo(2)–C(18)	1.986(11)	O(8)–C(20)	1.157(12)
Mo(2A)–Sn(2)	2.860(1)	N(1)–C(8)	1.442(10)
Sn(1)–C(39)	2.161(8)	N(1)–C(7)	1.452(10)
Sn(2)–C(39)	2.149(8)	C(8)–C(9)	1.523(11)
O(1)–C(6)	1.221(9)	C(9)–C(10)	1.489(11)
Bond angles			
C(33)–Sn(1)–C(39)	113.9(3)	N(1)–C(7)–C(6)	115.2(7)
C(39)–Sn(1)–C(27)	103.6(4)	N(1)–C(8)–C(9)	115.4(7)
C(39)–Sn(1)–Mo(1)	107.7(2)	O(2)–C(9)–C(10)	120.4(7)
C(40)–Sn(2)–C(39)	111.8(3)	O(2)–C(9)–C(8)	122.6(7)
C(40)–Sn(2)–Mo(2A)	115.2(2)	C(10)–C(9)–C(8)	117.0(7)
C(39)–Sn(2)–Mo(2A)	105.8(2)	C(11)–C(10)–C(9)	124.4(7)
C(21)–N(1)–C(8)	121.3(7)	C(14)–C(10)–C(9)	127.8(7)
C(21)–N(1)–C(7)	122.8(7)	O(3)–C(15)–Mo(1)	175.4(8)
C(8)–N(1)–C(7)	115.2(7)	O(4)–C(16)–Mo(1)	177.7(9)
C(1)–C(5)–C(6)	127.0(7)	O(5)–C(17)–Mo(1)	174.6(7)
C(4)–C(5)–C(6)	124.8(7)	O(6)–C(18)–Mo(2)	177.2(8)
O(1)–C(6)–C(5)	123.0(7)	O(7)–C(19)–Mo(2)	178.0(9)
O(1)–C(6)–C(7)	120.6(8)	O(8)–C(20)–Mo(2)	175.7(10)
C(5)–C(6)–C(7)	116.4(7)	Sn(1)–C(39)–Sn(2)	123.4(4)
Torsion angles			
C(1)–C(5)–C(6)–O(1)	–173.8(8)	O(2)–C(9)–C(10)–C(14)	–172.8(8)
C(4)–C(5)–C(6)–O(1)	5.7(12)	O(2)–C(9)–C(10)–C(11)	4.6(12)

Symmetric operations of "A" are $1 - x, y, 1.5 - z$.

$\mu-[\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}=\text{N}=\text{C}(\text{S})\text{C}_4\text{H}_3\text{S}]\text{Mo}(\text{CO})_3\text{SnCl}_2$ (2.7300(7) Å) [11]). The C(1)–C(5) cyclopentadienyl plane and the C(10)–C(14) cyclopentadienyl plane, with the dihedral angle of 98.2°, are closely perpendicular to each other. In addition, the carbonyl group π -systems have good coplanarity with the adjacent cyclopentadienyl planes. The C(6)O(1) carbonyl slightly deviates from the C(1)–C(5) cyclopentadienyl plane, with a value of only 0.0538 Å for O(1) and –0.0361 Å for C(6), respectively. It is worthy to point out that the angle $\angle\text{Sn}(1)\text{–C}(39)\text{–Sn}(2)$ (123.4(4)°) is larger than the corresponding angle $\angle\text{Sn}\text{–C}\text{–Sn}$ (117.8(5)°) in the 14-membered terephthaloyl bridging cyclopentadienyl complex $\{p-[(\text{CO})_3\text{MoC}_5\text{H}_4\text{C}(\text{O})_2\text{C}_6\text{H}_4]\{(\text{Ph}_2\text{Sn})_2\text{CH}_2\}\}$ [7b], and significantly away from the angle in the tetrahedral geometry of the sp^3 hybridized carbon, indicating that complex 7 possibly has bigger ring strain.

In conclusion, N-bridging cyclopentadienyl metal dianions $[\text{PhN}(\text{CH}_2\text{COCpM}(\text{CO})_3)_2]^{2-}$ (M = Mo or W) can be easily obtained. Reaction of these flexibly bridged metal dianions with $\text{CH}_2(\text{SnPh}_2\text{Br})_2$ is markedly different from that of the rigid terephthaloyl analogues, and the former

results in novel 24-membered octanuclear heterodimetallic organometallamacrocycles involving metal–metal bonds as the integral parts of the molecular architecture.

3. Experimental

All reactions were carried out under an argon atmosphere using standard Schlenk and Cannula techniques. Diglyme, hexane, ether and THF were distilled from sodium and benzophenone ketyl prior to use. NMR spectra were obtained on a Bruker AV300 spectrometer using CDCl_3 as solvent, and the chemical shifts were reported in ppm with respect to the reference. IR spectra data were obtained from a Bruker Equinox 55 spectrometer using KBr discs. Elemental analyses were carried out on an Elementar Vairo EL analyzer. $\text{PhN}(\text{CH}_2\text{CO}_2\text{Et})_2$ [12] and $\text{CH}_2(\text{SnPh}_2\text{Br})_2$ [13] were prepared by the published methods.

3.1. Preparation of $\text{PhN}(\text{CH}_2\text{COCpNa})_2$

To the solution of cyclopentadienyl sodium in 40 ml of THF, prepared from the reaction of cyclopentadiene (9.00 ml, 110 mmol) with Na (2.30 g, 100 mmol), was added dropwise $\text{PhN}(\text{CH}_2\text{CO}_2\text{Et})_2$ (13.3 g, 50.0 mmol) at room temperature. After addition, the reaction mixture was stirred and refluxed for 20 h. During this period, brown-yellow precipitation was formed gradually. Cooling to room temperature, the precipitation was filtered off, washed with absolute ether, and dried in vacuum to yield brown-yellow solid of $\text{PhN}(\text{CH}_2\text{COCpNa})_2$ (14.3 g, 82%).

3.2. Preparation of $\text{PhN}(\text{CH}_2\text{COCpMo}(\text{CO})_3\text{SnPh}_2\text{Cl})_2$ (3)

$\text{PhN}(\text{CH}_2\text{COCpNa})_2$ (87.0 mg, 0.250 mmol) was added to the solution of $\text{Mo}(\text{CO})_6$ (132 mg, 0.500 mmol) in 30 ml of THF. The mixture was stirred and refluxed for 20 h to obtain a black-red solution of $\text{PhN}(\text{CH}_2\text{COCpMo}(\text{CO})_3\text{Na})_2$ (1). After it was cooled to room temperature, Ph_2SnCl_2 (172 mg, 0.500 mmol) was added to the above solution, and the reaction mixture was stirred overnight at room temperature. The solvent was removed under a reduced pressure and the residual solid was extracted with CH_2Cl_2 . The extracted solution was passed through a short neutral alumina column eluted with CH_2Cl_2 to obtain a yellow solution. After removing the solvent, the residual solid was recrystallized from CH_2Cl_2 /hexane to yield the solids of 3. Yield: 100 mg (31%). ^1H NMR: δ 7.65, 7.42 (m, m, 8H, 12H, SnC_6H_5), 7.21, 6.81, 6.55 (t, t, d, $J = 7.2$ Hz, 7.2 Hz, 8.4 Hz, 2H, 1H, 2H, NC_6H_5), 5.98, 5.47 (t, t, 4H, 4H, overlapped AA'BB' system in C_5H_4), 4.24 (s, 4H, CH_2). ^{13}C NMR: δ 58.8 (CH_2), 91.2, 94.5, 100.9 (C_5H_4), 113.5, 119.6, 129.3, 129.7, 130.2, 135.0, 144.7, 148.0 (SnC_6H_5 and NC_6H_5), 193.2 ($\text{C}=\text{O}$), 221.8, 225.5 ($\text{C}\equiv\text{O}$). IR: $\nu_{\text{C}=\text{O}} = 2015.1$ (vs), 1955.5 (s), 1916.4 (vs); $\nu_{\text{C}=\text{O}} = 1697.3$ (s) cm^{-1} . Anal. Calc. for

$\text{C}_{50}\text{H}_{37}\text{Cl}_2\text{Mo}_2\text{NO}_8\text{Sn}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 45.86; H, 2.90; N, 1.06. Found: C, 45.87; H, 3.00; N, 1.01%.

3.3. Preparation of $\text{PhN}(\text{CH}_2\text{COCpMo}(\text{CO})_3\text{SnPh}_2\text{Br})_2$ (4)

This complex was obtained similarly using Ph_2SnBr_2 instead of Ph_2SnCl_2 to react with 1 as described above for 3. After similar workup, yellow solids of 4 were obtained. Yield: 130 mg (38%). ^1H NMR: δ 7.58, 7.33 (m, m, 8H, 12H, SnC_6H_5), 7.14, 6.74, 6.48 (t, t, d, $J = 7.8$ Hz, 7.2 Hz, 8.1 Hz, 2H, 1H, 2H, NC_6H_5), 5.91, 5.40 (t, t, 4H, 4H, overlapped AA'BB' system in C_5H_4), 4.33 (s, 4H, CH_2). ^{13}C NMR: δ 58.2 (CH_2), 90.1, 93.3, 99.6 (C_5H_4), 113.3, 119.2, 128.7, 128.9, 129.5, 136.5, 141.8, 148.0 (SnC_6H_5 and NC_6H_5), 193.1 ($\text{C}=\text{O}$), 222.5 ($\text{C}\equiv\text{O}$). IR: $\nu_{\text{C}=\text{O}} = 2014.8$ (vs), 1956.3 (s), 1917.0 (vs); $\nu_{\text{C}=\text{O}} = 1697.2$ (s) cm^{-1} . Anal. Calc. for $\text{C}_{50}\text{H}_{37}\text{Br}_2\text{Mo}_2\text{NO}_8\text{Sn}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 42.13; H, 2.70; N, 0.96. Found: C, 41.96; H, 2.77; N, 1.05%.

3.4. Preparation of $\text{PhN}(\text{CH}_2\text{COCpW}(\text{CO})_3\text{SnPh}_2\text{Cl})_2$ (5)

$\text{PhN}(\text{CH}_2\text{COCpNa})_2$ (87.0 mg, 0.250 mmol) was added to the solution of $\text{W}(\text{CO})_6$ (176 mg, 0.500 mmol) in 30 ml of diglyme. The mixture was stirred and refluxed for 6 h to obtain a black-red solution of $\text{PhN}(\text{CH}_2\text{COCpW}(\text{CO})_3\text{Na})_2$ (2). The mixture was cooled to room temperature and Ph_2SnCl_2 (172 mg, 0.500 mmol) was added to the solution, and the reaction mixture was stirred overnight at room temperature. After similar workup employed for the isolation of 3, yellow solids of 5 were obtained. Yield: 110 mg (30%). ^1H NMR: δ 7.64, 7.43 (m, m, 8H, 12H, SnC_6H_5), 7.21, 6.82, 6.55 (t, t, d, $J = 7.6$ Hz, 7.6 Hz, 8.0 Hz, 2H, 1H, 2H, NC_6H_5), 6.03, 5.58 (t, t, 4H, 4H, overlapped AA'BB' system in C_5H_4), 4.41 (s, 4H, CH_2). ^{13}C NMR: δ 58.6 (CH_2), 88.9, 93.2, 99.4 (C_5H_4), 113.5, 119.6, 129.1, 129.6, 130.0, 135.0, 143.7, 147.8 (SnC_6H_5 and NC_6H_5), 192.4 ($\text{C}=\text{O}$), 210.5, 212.6 ($\text{C}\equiv\text{O}$). IR: $\nu_{\text{C}=\text{O}} = 2009.8$ (vs), 1945.4 (vs), 1907.7 (vs); $\nu_{\text{C}=\text{O}} = 1699.4$ (s) cm^{-1} . Anal. Calc. for $\text{C}_{50}\text{H}_{37}\text{Cl}_2\text{NO}_8\text{Sn}_2\text{W}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 40.48; H, 2.56; N, 0.93. Found: C, 40.74; H, 2.64; N, 1.05%.

3.5. Preparation of $\text{PhN}(\text{CH}_2\text{COCpW}(\text{CO})_3\text{SnPh}_2\text{Br})_2$ (6)

This complex was obtained similarly using Ph_2SnBr_2 instead of Ph_2SnCl_2 to react with 2 as described above for 5. After similar workup, yellow solids of 6 were obtained. Yield: 120 mg (31%). ^1H NMR: δ 7.63, 7.42 (m, m, 8H, 12H, SnC_6H_5), 7.21, 6.83, 6.55 (t, t, d, $J = 8.1$ Hz, 7.2 Hz, 8.1 Hz, 2H, 1H, 2H, NC_6H_5), 6.03, 5.58 (t, t, 4H, 4H, overlapped AA'BB' system in C_5H_4), 4.40 (s, 4H, CH_2). ^{13}C NMR: δ 58.7 (CH_2), 89.1, 94.0, 99.3 (C_5H_4), 113.5, 119.7, 129.0, 129.6, 130.0, 135.2,

142.6, 147.7 (SnC₆H₅ and NC₆H₅), 192.4 (C=O), 210.8, 212.9 (C≡O). IR: $\nu_{\text{C=O}} = 2010.8$ (vs), 1946.5 (s), 1907.8 (vs); $\nu_{\text{C=O}} = 1698.5$ (s) cm^{-1} . Anal. Calc. for C₅₀H₃₇Br₂NO₈Sn₂W₂ · 0.5CH₂Cl₂: C, 38.21; H, 2.41; N, 0.88. Found: C, 38.01; H, 2.90; N, 0.80%.

3.6. Preparation of

[PhN(CH₂COCpMo(CO)₃)₂]₂[(SnPh₂)₂CH₂]₂ (7)

This complex was obtained similarly using CH₂(SnPh₂Br)₂ (180 mg, 0.250 mmol) instead of Ph₂SnCl₂ (172 mg, 0.500 mmol) to react with **1** as described above for **3**. After similar workup, yellow solids of **7** (recrystallized from ClCH₂CH₂Cl/heptane) were obtained. Yield: 138 mg (45%). ¹H NMR: δ 7.26–7.07 (m, 22H, SnC₆H₅ and NC₆H₅), 6.65–6.56 (m, 3H, NC₆H₅), 5.64, 4.80 (m, m, 4H, 4H, C₅H₄), 4.57 (s, 4H, NCH₂), 1.45 (s, 2H, SnC H₂). ¹³C NMR: δ 25.5 (SnCH₂), 60.0 (SnCH₂), 91.6, 93.5, 102.8 (C₅H₄), 114.2, 120.6, 130.6, 131.8, 132.2, 133.1, 138.8, 150.8 (SnC₆H₅ and NC₆H₅), 196.2 (C=O), 229.0 (C≡O). IR: $\nu_{\text{C=O}} = 1995.6$ (vs), 1928.0 (s), 1892.1 (vs); $\nu_{\text{C=O}} = 1694.0$ (s) cm^{-1} . Anal. Calc. for C₁₀₂H₇₈Mo₄N₂O₁₆Sn₄ · 2ClCH₂CH₂Cl: C, 48.15; H, 3.28; N, 1.06. Found: C, 47.86; H, 2.90; N, 1.42%.

3.7. Preparation of

[PhN(CH₂COCpW(CO)₃)₂]₂[(SnPh₂)₂CH₂]₂ (8)

This complex was obtained similarly using CH₂(SnPh₂Br)₂ (180 mg, 0.250 mmol) instead of Ph₂SnCl₂ (172 mg, 0.500 mmol) to react with **2** as described above for **5**. After similar workup, yellow solids of **8** (recrystallized from ClCH₂CH₂Cl/heptane) were obtained. Yield: 133 mg (38%). ¹H NMR: δ 7.18–6.91 (m, 22H, SnC₆H₅ and NC₆H₅), 6.59–6.52 (m, 3H, NC₆H₅), 5.59, 4.82 (m, m, 4H, 4H, C₅H₄), 4.47 (s, 4H, NCH₂), 1.28 (s, 2H, SnCH₂). ¹³C NMR: δ 22.7 (SnCH₂), 57.3 (SnCH₂), 89.4, 90.5, 93.0 (C₅H₄), 111.4, 118.0, 127.7, 128.0, 128.5, 129.5, 136.1, 147.9 (SnC₆H₅ and NC₆H₅), 192.8 (C=O), 214.1 (C≡O). IR: $\nu_{\text{C=O}} = 1990.3$ (vs), 1918.5 (s), 1877.4 (vs); $\nu_{\text{C=O}} = 1696.7$ (m) cm^{-1} . Anal. Calc. for C₁₀₂H₇₈N₂O₁₆Sn₄W₄: C, 43.79; H, 2.81; N, 1.00. Found: C, 44.27; H, 3.34; N, 1.02%.

3.8. Preparation of PhN(CH₂COCpMo(CO)₃SnPh₂)₂S (9)

The solution of Na₂S · 9H₂O (17.3 mg, 0.0720 mmol) in 5 ml of ethanol was added dropwise to the solution of **3** (92.0 mg, 0.0720 mmol) in 10 ml of THF. The mixture was stirred and refluxed for 3 h. After it was cooled to room temperature, the solvent was removed under a reduced pressure and the residual solid was extracted with CH₂Cl₂. The extracted solution was passed through a short neutral alumina column eluted with CH₂Cl₂ to obtain a yellow solution. After removing the solvent, the residual solid was recrystallized from CH₂Cl₂/hexane to yield yellow

Table 2

Crystal data and refinement parameters for 7 · 6ClCH₂CH₂Cl

Formula	C ₁₁₄ H ₁₀₂ Cl ₁₂ Mo ₄ N ₂ O ₁₆ Sn ₄
Formula weight	3039.90
Crystal size (mm)	0.24 × 0.20 × 0.18
Crystal system	Monoclinic
Space group	C2/c
<i>Cell parameters</i>	
<i>a</i> (Å)	24.196(9)
<i>b</i> (Å)	22.286(8)
<i>c</i> (Å)	22.186(8)
β (°)	91.577(5)
<i>V</i> (Å ³)	11959(8)
<i>Z</i>	4
<i>T</i> (K)	113(2)
<i>d</i> _{calc} (g cm ⁻³)	1.688
<i>F</i> (000)	6000
λ (Mo K α) (Å)	0.71070
μ (mm ⁻¹)	1.556
Number of reflections measured	44756
Number of reflections observed	9254 (<i>I</i> ≥ 2 σ (<i>I</i>))
Number of parameters	722
Residuals <i>R</i> , <i>wR</i>	0.0713, 0.1789
Goodness-of-fit on <i>F</i> ²	1.087

solids of **9**. Yield: 27.0 mg (30%). ¹H NMR: δ 7.26, 7.13–6.97 (m, m, 8H, 14H, SnC₆H₅ and NC₆H₅), 6.66, 6.35 (t, d, *J* = 7.2 Hz, 8.1 Hz, 1H, 2H, NC₆H₅), 5.95 (t, *J* = 2.1 Hz, 4H, C₅H₄), 5.00 (m, 8H, C₅H₄ and CH₂). IR: $\nu_{\text{C=O}} = 2005.1$ (vs), 1941.5 (s), 1907.4 (vs); $\nu_{\text{C=O}} = 1705.8$ (m) cm^{-1} . Anal. Calc. for C₅₀H₃₇Mo₂NO₈SSn₂: C, 48.38; H, 3.00; N, 1.13. Found: C, 48.78; H, 3.00; N, 1.16%.

3.9. X-ray crystallography

Crystals of **7** suitable for X-ray analysis were obtained from a ClCH₂CH₂Cl/heptane solution at –18 °C. The part of incorporated solvents was quickly eliminated when the crystals were taken out of the solvent phase, so the single crystal of complex **7** was quickly mounted with viscous oil and cooled to the data collection temperature (113 K). One ClCH₂CH₂Cl molecule (C(56), C(57), Cl(5) and Cl(6)) were found to be disorder. The satisfactory results were obtained when C(56), C(57), Cl(5) and Cl(6) were given occupancy factors of 0.63 and C(56)', C(57)', Cl(5)' and Cl(6)' were given occupancy factors of 0.37. Intensity data were collected on a Rigaku Saturn CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71070$ Å) using the $\omega/2\theta$ scan technique. The structures were solved by direct methods and refined by full-matrix least-squares on *F*². All non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for **7** is listed in Table 2.

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Appendix A. Supplementary material

CCDC 653240 contains the supplementary crystallographic data for 7. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.10.002](https://doi.org/10.1016/j.jorganchem.2007.10.002).

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